
Duwamish River Basin, Combined Sewer Overflow Survey

Sampling and Analysis Plan

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DRAFT



King County

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Duwamish River Basin Combined Sewer Overflow Survey Sampling and Analysis Plan

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EXECUTIVE SUMMARY

This plan describes the sampling and analytical methods chosen to survey at least two, and possibly additional points, within the combined sewer collection system for PCBs and other contaminants. These combined waters are intended to represent what may discharge into the Duwamish River from the Duwamish Diagonal CSO. This survey will not sample an actual CSO event, but will instead serve as a starting point to understand potential PCB, SVOC, and other contaminant inputs from CSO-like effluents to the Duwamish River.

1.0. INTRODUCTION

This sampling and analysis plan (SAP) presents project information and sampling and analytical methodologies. These will be employed to perform a survey of chemical and conventional parameters in waters representing combined sewer overflow (CSO) conditions within the Duwamish River Basin. Figures referenced in the SAP narrative are included as Appendix A.

1.1 Project Background

In Winter 2003, King County conducted a removal action of contaminated sediments off the Diagonal/Duwamish (D/D) Combined Sewer Overflow/Storm Drain (CSO/SD) for the Elliott Bay Duwamish Restoration Program (EBDRP). The removal was conducted by dredging and the area was capped in January 2004. In February 2005, a thin-layer placement of sand was added to a 4-acre area around the southwest portion of the original dredge site to reduce exposure to residual PCBs. King County has collected surface sediments as part of the monitoring required for this action. As of 2006, these samples have indicated recontamination of polychlorinated biphenyl (PCB) and bis(2-ethylhexyl)phthalate (DEHP) in the sediments near the CSO/SD outfall.

King County completed a Water Quality Assessment (WQA) of the Duwamish River and Elliott Bay in 1999 to evaluate the effects of combined sewer overflows (CSOs) in these water bodies. For this assessment, CSOs were sampled for a variety of chemical and conventional parameters. Data from these samples were used in the Environmental Fluids Dynamic Computer Code (EFDC) model, a hydrodynamic and fate and transport numerical model that was used as part of WQA to estimate chemical concentrations under conditions both with and without CSO discharges. Some analytes, such as PCBs, were not detected in CSOs; however, methods available at that time were not capable of measuring these chemicals at low levels in water.

King County Wastewater Treatment Division (WTD) would like to better understand the current levels of certain chemicals and conventional parameters in the Duwamish River Basin CSO system. These data will assist in understanding if CSO discharges or stormwater discharges could be related to PCB and DEHP levels observed on the D/D area cap. A secondary use of these data by WTD is to assess concentrations of certain parameters in CSOs to help evaluate pilot treatment projects.

1.2 Survey Scope of Work

This survey will involve collection and analysis of in-pipe water samples from two locations, at a minimum, in the collection system of the Duwamish River Basin. Because of the difficulty in sampling actual CSO events, samples will be collected to represent partially- to near-full conditions of combined sewers collection system. These locations will be from

combined sewers collection system in portions of the King County sewerage system that could potentially discharge to the Duwamish/Diagonal CSO/SD Outfall or other Duwamish River CSOs during a combined sewer overflow (CSO) event.

A goal of sampling at least three events will occur during between September 2007 and May 2008. Samples will be analyzed for PCB congeners, SVOCs, select metals, and several conventional water quality parameters, depending on sample volume.

1.3 Survey Schedule

Three sampling events will occur between September 2007 and May 2008. The specific sampling day and time is dependant on wet weather and combined sewer system conditions. CSO type conditions occur in the locations being sampled, however it is very difficult to predict, even based on rainfall conditions, when a CSO may occur. The collection system is designed to prevent CSO events to the maximum extent possible. Therefore, samples will be collected from within the combined sewers.

PCB congener samples will be shipped to Axys Analytical at KCELS discretion, based on weather patterns and packaging. The expected turn-around time for congener analysis is 60 to 90 days from receipt. KCEL will try to expedite result delivery. The turnaround time for all other analytical data is approximately six to eight weeks from the date of sample collection. It is anticipated that data from all sampling events will be validated, reviewed, and ready for release by winter 2008.

1.4 Project Staff

The following staff are responsible for project execution:

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2.0. SURVEY DESIGN

The goal of King County's CSO survey is to collect samples that represent CSO conditions from the Duwamish River Basin and to analyze these samples for 209 PCB congeners, SVOCs, select metals and conventional parameters. Resulting data will allow King County to further characterize concentrations of these parameters in CSO conditions for the Duwamish Estuary. These data can be used in source control evaluations for D/D CSO/SD and secondarily to evaluate CSO conditions for future pilot treatment study.

2.1 Data Quality Objectives

The data quality objectives (DQOs) are to collect data of known and sufficient quality to meet the survey goals. Validation of project data will assess whether the data collected are of sufficient quality to meet the survey goals. The data quality issues of precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity are described in the following sections, along with data validation.

2.1.1 Precision, Accuracy, and Bias

Precision is the agreement of a set of results among themselves and is a measure of the ability to reproduce a result. Accuracy is an estimate of the difference between the true value and the measured value. The accuracy of a result is affected by both systematic and random errors. Bias is a measure of the difference, due to a systematic factor, between an analytical result and the true value of an analyte. Precision, accuracy, and bias for analytical chemistry may be measured by one or more of the following quality control (QC) procedures:

- analysis of various laboratory QC samples such as blanks, surrogates, and replicates; and
- collection and analysis of field replicate samples.

Because this project is a survey, and CSOs are known to be highly variable in their discharge frequency and rate, precision is expected to be low. Precision of replicates is expected to be within 50%, although this matrix has not been evaluated by the selected methods before. If precision is considered too low for project needs, these data will be used to guide future sampling efforts.

Accuracy, for PCB congener data is not quantifiable since certified reference materials do not exist for CSO effluents. However, the isotopic dilution method chosen for this study is the most rigorous method for PCB congener analysis. This method uses isotopically labeled PCBs to track the recovery performance of the range of PCB homologs. Thus, each congener concentration is theoretically adjusted for the analytical performance of that specific sample/sample matrix.

Since this study intends to represent CSO conditions, and those conditions vary in both time and space, analytical bias from an actual CSO event cannot be quantified. However, composite samplers will be used to retrieve samples of CSO-like waters during rainfall conditions from pipes in the Duwamish River watershed.

2.1.2 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at the sampling point, or an environmental condition. Water samples will be collected from locations within the combine sewer system to represent CSO conditions. The selected locations have discharged to the D/D CSO in the past under varying rainfall and conveyance conditions (i.e., pump status). The frequency these locations actually overflow to the Duwamish is variable and somewhat unpredictable. Therefore, to make efficient use of resources, samples will be collected via a water level triggered auto sampler. The auto samplers will be set to collect samples from pipes, which represent waters that may discharge via the CSO under certain system conditions. Effluent from an actual CSO event will not be collected.

2.1.3 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable analytical data are generated, compared to the total number of samples submitted for analysis. Sampling with adherence to standardized sampling and testing protocols will aid in providing a complete set of data for this survey. The goal for completeness is 90%. If 90% completeness is not achieved, the project team will evaluate if the DQOs can still be met or if additional samples may need to be collected and analyzed.

2.1.4 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through using standard techniques to collect and analyze representative samples, along with standardized data validation and reporting procedures. By following the guidance of this SAP, the goal of comparability between this and future sampling events will be achieved. Historical CSO data may be compared with data generated from this survey to enhance data analysis efforts. Previous data will be used if comparable sampling and/or analytical techniques were employed. Previous sampling efforts have analyzed CSO effluents by similar conventionals and metals methods. However, PCB congeners have not been analyzed in CSO effluents before, thus these data will have limited comparability to other King County data.

2.1.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the survey goal. The analytical method detection limits presented in Section 5 are sensitive enough to detect PCB

congeners and other analytes at concentrations of interest to understand contaminant inputs to the Duwamish River from CSOs.

2.1.6 Data Validation

Chemical data generated during this survey will be validated according to accepted Environmental Protection Agency (EPA) guidelines (EPA 2001), where applicable. For PCB congeners, the validation will use the criteria and acceptance limits defined in Method 1668A and this SAP. The subcontracted analytical laboratory will supply data packages allowing for this level of validation. All other chemical analysis and associated conventional water quality data will be validated against requirements of the reference methods as well as the requirements of this SAP.

2.2 Sampling and Analytical Strategy

The CSO survey sampling strategy has been design to employ the knowledge of the collection system obtained through IW and WTD monitoring programs. Thus, three sampling events will comprise this study and will provide enough data to meet the survey goal while minimizing costs and impacts to staff and laboratory capacity. Additional samples will be collected if time and budget allow. Samples will be collected from the combined system under conditions that represent CSO conditions by sampling partial full conditions of combined sewers. Samples will be collected at two or three locations during each sampling event and all samples will be submitted for PCB congener and select conventional water quality analyses. Actual sample volume (if less than needed) will dictate if SVOCs, select metals and remaining conventional parameters can be measured for all sampling events.

Samples will be collected from at least two locations: combined sewer access points “A00602” and “A4007” are both within the Duwamish watershed and both may contribute to overflow events. Due to limitations in sampling gear, staff and locations that can be accessed for CSO type conditions within the collection system of the Duwamish Basin, only two locations are targeted at this time. If the methods outlined in Section 3.0 below are successful, additional samples maybe collected in other locations of the Duwamish Basin. Where possible, a field replicate sample will be collected during a collection event. Additionally, one field blank will be collected in the field prior to each sampling event. Field blanks will be collected by using an autosampler to remove a sufficient quantity of de-ionized water from a carboy supplied by KCEL. The conventional parameters of temperature, pH, and conductivity should be measured in the sampled waters at the time the carboy is retrieved from the autosampler.

2.2.1 Sampling Station Locations and Sample Identification

The two initial sampling station locations will initially be the Duwamish Siphon – Forebay (Locator A00602) and Michigan Street Regulator (Locator A4007) as shown in Figure 1. Additional locations may be sampled once three events have occurred at these two locations.

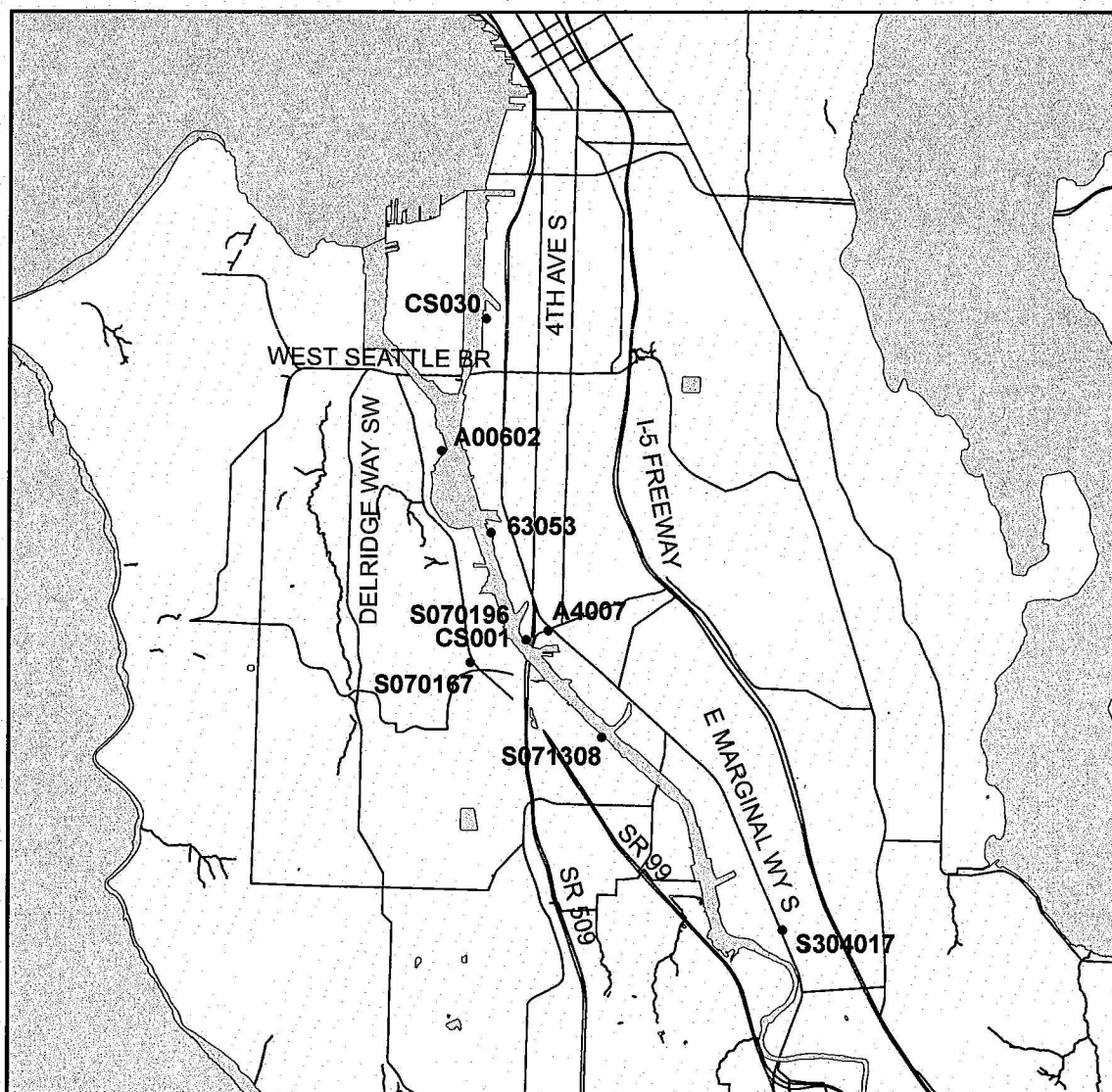


Figure 1. Sampling locations for CSO-like waters

- Michigan Street Regulator: A King County CSO is located near the intersection of Hanford Street and Rainier Avenue (Hanford #1). Discharges to the Duwamish/Diagonal CSO/SD can occur at this location when the Hanford Trunk Line

or the nearby Bayview Tunnel become full with excess stormwater inputs into the combined sewer system.

- Duwamish Siphon, Forebay: Another potential CSO discharge location near the Duwamish/Diagonal CSO/SD Outfall is the overflow relief structure on the east side of the Duwamish Siphon. The invert elevation of this relief structure is lower than critical components of the nearby Duwamish Pump Station. This elevation differential prevents the pump station from being impacted by wastewater in the event of some catastrophic system failure. Overflows from this relief structure occur when the nearby Elliot Bay Interceptor is full or near-full.

Samples will be identified using the sample location or locator name and the date of collection.

Table 1. Potential CSO-like pipe sampling locations in the Duwamish Basin

Locator	Sampling priority	Locator Description	Northing	Easting
A4007	1	Michigan St. Regulator	202231	1270402
A00602	1	Duwamish Siphon, Forebay	209100	1266278
CS030	1	Hanford St CSO (aka Hanford #2 CSO)	214147	1267988
063053	2	Brandon St. CSO	205961	1268192
S070167	2	W. Michigan Reg/CSO (W042)	201021	1267395
S070196	2	S. Michigan CSO (W039)	201878	1269562
CS001	3	Michigan CSO (S. Michigan)	201878	1269562
S071308	3	8 th Ave S. Reg/CSO	198151	1272447
S304017	3	Norfolk Reg/CSO	190791	1279389
A00601	4	Duwamish Siphon, Aftbay	NA	NA
Not created	4	Lander II Reg/CSO	NA	NA

2.2.2 Sample Acquisition and Analytical Parameters

Sampling will be conducted by King County Environmental Services field group using Isco® Autosamplers. Sampling techniques are discussed in Section 3.

Each sample will be analyzed for 209 PCB congeners along with the following conventional parameters; dissolved organic carbon (DOC), total organic carbon (TOC), and total suspended solids (TSS). If adequate sample volume is available, samples will also be analyzed for SVOCs, selected metals shown below and additional conventional parameters (COD, VSS, ammonia, total phosphorus, and nitrogen.). PCB congener analysis will be conducted by Axys Analytical in Sidney, British Columbia. All other chemical analyses and conventional analyses will be conducted by the King County Environmental Laboratory.

Table 2. Metals analysis by ICP-MS

Analyte	Analyte (con't)
Total Arsenic (As)	Manganese (Mn)
Cadmium (Cd)	Nickel (Ni)
Total Chromium (Cr)	Silver (Ag)
Calcium (Ca)	Magnesium
Copper (Cu)	Zinc (Zn)
Lead (Pb)	Iron

3.0. SAMPLING PROCEDURES

This section describes the sampling procedures that will be followed over the course of all sampling events to meet the survey DQOs: representativeness, comparability, and completeness. Equipment and sample preparation will generally follow PSAMP (1997) protocols.

3.1 Sampler Decontamination and Sample Collection

Auto samplers will be fitted with new and pre-cleaned silicon tubing in the peristaltic pump for each sampling event. Teflon tubing and stainless steel (SS) fittings shall be used for all other tubing runs. Teflon tubing and autosample containers shall be cleaned with: (1) alconox or other suitable laboratory detergent; (2) a H₂SO₄ rinse; (3) a DI water rinse; and (4) an acetone rinse. All SS fittings and connectors are cleaned in the same manner except they are not subjected to the acid rinse step. Composite autosampler bottles and autosampler tubing will be cleaned prior to each sampling event according to laboratory standard operating procedures (SOP # 02-02-014-001) for collecting samples for low-level analysis using autosamplers.

Auto samplers will be automatically triggered by water depth in each sampled pipe. Minimum water depth to initiate sampling should be approximately 60% of full depth. Sampling will continue as long as water depths remain above this level. The sample will be collected continuously over two hours. The two-hour time frame was selected to balance against: (1) the risk of flows changing and representing something other than potential CSO overflow conditions; (2) the degradation of analytes in stored aliquots; and (3) a suitably long time frame to generally characterize contaminant masses.

Sample containers used for shipment of waters to the contract laboratory will precleaned to EPA specifications by the contract laboratory.

3.2 Sample Delivery and Storage

All samples (in autosampler carboys) will be kept in ice-filled coolers until delivery to the King County Environmental Laboratory, on the same day that they were collected. Because auto samplers will be setup to automatically initiate sampling, samples cannot be refrigerated during the compositing process. Additional sample preservation, if required, will be performed upon receipt of the samples at the King County Environmental Laboratory. Samples will be split from the glass autosampler container into the appropriate analytical containers and preserved according to method specifications at the laboratory.

PCB congener samples will be shipped to Axys Analytical via overnight express delivery service. Actual shipping date may vary depending on whether additional samples are

expected shortly and packaging limitations. Table 2 shows sample handling and storage requirements.

Table 3. Sample Container, Preservation, Storage, and Hold Time Requirements in

Analyte	Container	Preservation	Storage	Hold Time
PCB Congeners	2 x 1-L amber glass	None	refrigerate at 4°C in the dark	1 year
Total Organic Carbon	2 x 40-ml amber VOA	H3PO4 to pH<2	refrigerate at 4°C	28 days
Total Suspended Solids	1-L clear HDPE	None	refrigerate at 4°C	7 days
- Volatile Suspended Solids	- (together with TSS)	None	refrigerate at 4°C	7 days
SVOCs	2 x 1L amber glass	None	refrigerate at 4°C	7/40 ²
Metals (Total & Dissolved)	500 mL Acid washed HDPE	HNO3 to pH<2	n/a	180 days
Mercury	- (from same 500mL container above)	HNO3 to pH<2	n/a	28 days
Mercury	Acid washed HDPE	HNO3 to pH<2	n/a	28 days
Chemical Oxygen Demand	125mL clear HDPE	H2SO4 to pH<2	refrigerate at 4°C	28 days
Ammonia N, nitrate-nitrite	250mL clear HDPE	Freeze filtered aliquot ¹	Freeze at -20°C	14 days
Total Nitrogen, Total Phosphorus	- (from same 250mL container above)	Freeze sample ³	Freeze at -20°C	28 days
Alkalinity	500mL clear HDPE	None	Refrigerate at 4°C	14 days
Minimum sample volume =	7,580 mL			

¹ Within 1 day of collection, samples must be filtered (.45 µm) prior to preservation.

² 7 days from sampling to extraction, 40 days from extraction to analysis

³ Samples must be frozen or preserved with H₂SO₄ within 2 days of collection

If additional sample matrix is available, the QC samples discussed in section 4 shall be conducted in the following priority: (1) SVOCs, (2) metals, (3) mercury, and (4) conventionals.

3.3 Chain of Custody

Chain of custody (COC) will commence at the time that each autosampler is deployed. The autosampler will be secured to ensure no tampering has occurred. Thus, all samples (carboys) will be under direct possession and control of King County field staff. For chain of custody purposes, closed/latched storm drains, autosamplers, and field vehicles will be considered “controlled areas.” All sample information will be recorded on a COC form (Figure 2). This form will be completed in the field and will accompany all samples during transport and delivery to the laboratory. Upon arrival at the King County Environmental Laboratory, the samples will be split in the appropriate containers then relinquished to the sample login person. The date and time of sample delivery will be recorded and both parties will then sign off in the appropriate sections on the COC form at this time. Once completed, original COC forms will be archived in the project file.

Samples delivered after regular business hours will be stored in a secure refrigerator until the next day. Samples delivered to Axys Analytical will be accompanied by a properly completed King County Environmental Laboratory COC form and custody seals will be placed on the shipping cooler. Axys Analytical will be expected to provide a copy of the completed COC form as part of their analytical data package.

3.4 Sample Documentation

Sampling information and sample metadata will be documented using the methods noted below.

- Field sheets generated by King County’s Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:
 1. sample ID number
 2. station name
 3. in-pipe station water depth at initiation and termination of auto sampling
 4. date and time of sample collection (start and end times of the compositing period)
 5. initials of all sampling personnel
- LIMS-generated container labels will identify each container with a unique sample number, station and site names, collect date, analyses required, and preservation method.

- The field sheet will contain records of collection times, general weather and the names of field crew.
- COC documentation will consist of the Lab's standard COC form, which is used to track release and receipt of each sample from collection to arrival at the lab.

3.5 Field Replicates

A field replicate will be collected during a sampling event at locations where two autosamplers can be installed and analyzed for all target parameters. Each field replicate will be collected from a separate auto sampler.

Collection and analysis of equipment/field blanks will be required for each sampling event. The following conditions apply to collection of the equipment blank sample:

- The equipment blank sample must be collected with the same tubing and sampling apparatus to be used to collect the samples for a given week.
- The equipment blank sample must be collected before the sampling begins.

As with the regular samples, the carboy with the equipment blank sample must be returned to KCEL for transfer of contents into the appropriate sample bottles. Equipment blanks shall be preserved, stored, and analyzed in the same manner as environmental samples.

4.0. ANALYTICAL METHODS AND DETECTION LIMITS

Analytical methods for PCB congener, SVOCs, metals, and conventional analyses are presented in this section, along with analyte-specific detection limits. For the SVOCs, metals and selected conventional analytes, the terms MDL and RDL, used in the following subsections, refer to method detection limit and reporting detection limit, respectively. The MDL is defined as the *minimum concentration of a chemical constituent that can be reliably determined with 99% confidence to be greater than zero* (40 CFR Part 136.2), while the RDL is defined as the *minimum concentration of a chemical constituent that can be reliably quantified* (also known as the practical quantitation limit) *within specified limits of precision and accuracy during routine laboratory operating conditions* (50 FR 46906, November 13, 1985).

The PCB congener data are reported down to the MDL value, which is determined for each sample based on the signal to noise ratio for each unique congener. Note that PCB congener data will be reported with MDL values only. Method 1668A defines a Minimum Level (ML) value for each congener. The ML value is used to evaluate levels in the method blank.

4.1 PCB Congeners

PCB congener analysis will follow Environmental Protection Agency (EPA) Method 1668A Revision A (EPA 2003), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. This method provides reliable analyte identification and very low detection limits. An extensive suite of labeled surrogate standards (Table 3) is added before samples are extracted. Data are “recovery-corrected” for losses in extraction and cleanup, and analytes are quantified against their labeled analogues.

Axys Analytical will perform this analysis according to their Standard Operating Procedure MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668, which is a proprietary document. The analytical procedure is summarized in the flow chart shown in Figure 4. A one-liter sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil and Alumina. Analysis is performed with an SPB Octyl column and a secondary DB1 column is used to resolve the co-eluting congeners PCB156 and PCB157. Method 1668A requires that if a sample contains more than 1% total solids, the solids and liquid will be extracted and analyzed separately.

Table 4. Labeled Surrogates and Recovery Standards Used for EPA Method 1668A PCB Congener Analysis

C₁₃-labeled PCB Congener Surrogate Standards				
1	37	123	155	202
3	54	118	167	205
4	81	114	156/157	208
15	77	105	169	206
19	104	126	188	209
C₁₃-labeled Cleanup Standards				
28	111	178		
C₁₃-labeled Internal (Recovery) Standards				
9	52	101	138	194

In addition to the surrogate, cleanup, and internal standards, which assess sample accuracy and bias, a method blank, laboratory duplicate, and an ongoing precision and recovery sample will be analyzed with each set of seven samples. Note that a matrix spike and matrix spike duplicate are not required, nor meaningful under Method 1668A.

- A **method blank** is an aliquot of a clean reference matrix (deionized, distilled water for water samples) that is processed through the entire analytical procedure. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results for all target analytes should be “less than the ML.” Method 1668A has specific requirements for method blanks that must be met before sample data can be reported (see section 9.5.2 of Method 1668A).
- A **laboratory duplicate** is a second aliquot of sample collected concurrently with the original autosampler composite. The laboratory duplicate is processed through the entire analytical procedure along with the original sample in the same quality control batch. Laboratory duplicate results are used to assess the precision of the analytical method and the relative percent difference between the results should be within method-specified or performance-based quality control limits.
- An **ongoing precision and recovery (OPR)** sample is to be analyzed with each QC sample batch. The OPR samples must show acceptable recoveries, according to Method 1668A, in order for samples to be analyzed and data to be reported.

- Table 4 lists the 209 PCB congeners and their respective target MDL values. The reported MDLs for individual samples may differ from those in Table 4 since they are determined by signal to noise ratios and changes to final volumes. Note that several of the congeners co-elute and a single result or MDL value is provided for the congeners in aggregate.

Table 5. PCB Congener detection limits by EPA method 1668a

PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)
CL1-PCB-1	3.57	CL4-PCB-48	6.07	CL5-PCB-107/124	23.1	CL6-PCB-164	5.22
CL1-PCB-2	8.94	CL4-PCB-49/69	18.6	CL5-PCB-109	23.3	CL6-PCB-165	10.5
CL1-PCB-3	4.56	CL4-PCB-50/53	21.0	CL5-PCB-110/115	14.9	CL6-PCB-167	5.85
CL2-PCB-4	8.62	CL4-PCB-52	12.0	CL5-PCB-111	8.55	CL6-PCB-169	6.65
CL2-PCB-5	5.83	CL4-PCB-54	7.00	CL5-PCB-112	4.55	CL7-PCB-170	11.2
CL2-PCB-6	9.28	CL4-PCB-55	8.28	CL5-PCB-114	4.26	CL7-PCB-171/173	31.0
CL2-PCB-7	113	CL4-PCB-56	5.83	CL5-PCB-118	7.44	CL7-PCB-172	6.68
CL2-PCB-8	4.72	CL4-PCB-57	6.56	CL5-PCB-120	6.62	CL7-PCB-174	11.2
CL2-PCB-9	4.96	CL4-PCB-58	10.9	CL5-PCB-121	8.80	CL7-PCB-175	10.2
CL2-PCB-10	7.19	CL4-PCB-59/62/75	21.1	CL5-PCB-122	8.38	CL7-PCB-176	5.91
CL2-PCB-11	13.4	CL4-PCB-60	7.26	CL5-PCB-123	11.4	CL7-PCB-177	5.92
CL2-PCB-12/13	7.16	CL4-PCB-61/70/74/76	18.3	CL5-PCB-126	6.29	CL7-PCB-178	5.56
CL2-PCB-14	5.07	CL4-PCB-63	6.70	CL5-PCB-127	6.51	CL7-PCB-179	8.24
CL2-PCB-15	6.62	CL4-PCB-64	60.8	CL6-PCB-128/166	10.6	CL7-PCB-180/193	23.0
CL3-PCB-16	6.73	CL4-PCB-66	4.46	CL6-PCB-129/138/160/163	11.0	CL7-PCB-181	13.0

PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)
CL3-PCB-17	7.11	CL4-PCB-67	6.38	CL6-PCB-130	7.90	CL7-PCB-182	7.27
CL3-PCB-18/30	10.6	CL4-PCB-68	6.25	CL6-PCB-131	17.5	CL7-PCB-183/185	21.1
CL3-PCB-19	6.49	CL4-PCB-72	4.64	CL6-PCB-132	10.9	CL7-PCB-184	5.22
CL3-PCB-20/28	7.85	CL4-PCB-73	10.7	CL6-PCB-133	8.58	CL7-PCB-186	11.0
CL3-PCB-21/33	6.42	CL4-PCB-77	5.35	CL6-PCB-134/143	14.3	CL7-PCB-187	12.7
CL3-PCB-22	4.71	CL4-PCB-78	5.28	CL6-PCB-135/151/154	13.4	CL7-PCB-188	3.75
CL3-PCB-23	5.02	CL4-PCB-79	4.56	CL6-PCB-136	7.20	CL7-PCB-189	7.07
CL3-PCB-24	6.40	CL4-PCB-80	6.81	CL6-PCB-137	14.6	CL7-PCB-190	6.49
CL3-PCB-25	3.87	CL4-PCB-81	8.26	CL6-PCB-139/140	22.1	CL7-PCB-191	11.6
CL3-PCB-26/29	5.10	CL5-PCB-82	5.80	CL6-PCB-141	5.47	CL7-PCB-192	9.31
CL3-PCB-27	6.66	CL5-PCB-83/99	36.0	CL6-PCB-142	11.7	CL8-PCB-194	5.44
CL3-PCB-31	6.39	CL5-PCB-84	11.1	CL6-PCB-144	6.01	CL8-PCB-195	9.98
CL3-PCB-32	4.57	CL5-PCB-85/116/117	11.8	CL6-PCB-145	10.7	CL8-PCB-196	12.3
CL3-PCB-34	6.68	CL5-PCB-86/87/97/108/119/125	78.7	CL6-PCB-146	8.10	CL8-PCB-197/200	11.3
CL3-PCB-35	3.83	CL5-PCB-88/91	37.4	CL6-PCB-147/149	12.6	CL8-PCB-198/199	22.1
CL3-PCB-36	2.59	CL5-PCB-89	5.60	CL6-PCB-148	7.48	CL8-PCB-201	9.06

PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)	PCB Congener	MDL (pg/L)
CL3-PCB-37	4.79	CL5-PCB-90/101/113	10.3	CL6-PCB-150	5.40	CL8-PCB-202	8.08
CL3-PCB-38	4.01	CL5-PCB-92	5.84	CL6-PCB-152	6.67	CL8-PCB-203	6.69
CL3-PCB-39	2.96	CL5-PCB-93/95/98/100/102	113	CL6-PCB-153/168	12.1	CL8-PCB-204	12.3
CL4-PCB-40/41/71	21.1	CL5-PCB-94	10.5	CL6-PCB-155	10.3	CL8-PCB-205	7.09
CL4-PCB-42	10.4	CL5-PCB-96	9.11	CL6-PCB-156/157	12.3	CL9-PCB-206	9.19
CL4-PCB-43	6.70	CL5-PCB-103	8.99	CL6-PCB-158	5.09	CL9-PCB-207	12.2
CL4-PCB-44/47/65	28.3	CL5-PCB-104	6.97	CL6-PCB-159	5.65	CL9-PCB-208	11.5
CL4-PCB-45/51	23.2	CL5-PCB-105	8.13	CL6-PCB-161	10.3	CL10-PCB-209	7.20
CL4-PCB-46	11.5	CL5-PCB-106	29.4	CL6-PCB-162	9.12		

MDL = method detection limit

pg/L = picograms per liter

4.2 SVOCs

Semivolatile organics will be prepared by liquid-liquid extraction as detailed in KCEL SOP 07-01-001-002, which is based upon EPA method 3520C. Briefly, samples may be stored for up to seven days at 40C. Before extraction, pH is adjusted with H₂SO₄ to approximately 2. Samples are then extracted with methylene chloride for 18 to 24 hours. Sample extracts will be concentrated using the KD apparatus to a volume of approximately 1 mL. Additional cleanup may be performed to ensure adequate instrument performance.

Following extraction and concentration, samples will be analyzed for the following list of compounds. Method detection limits and reporting limits are as shown.

Table 6. Method 3520C/625 SVOC Target Compounds and Reporting Limits in µg/L.

Analyte	MDL	RDL	Analyte	MDL	RDL
1,4-Dichlorobenzene	0.01	0.02	Dibenzo(a,h)Anthracene	0.02	0.04
2-Methylnaphthalene	0.02	0.04	Diethyl Phthalate	0.05	0.1
4-Methylphenol	0.1	0.2	Dimethyl Phthalate	0.05	0.1
Acenaphthene	0.02	0.04	Di-n-Butyl Phthalate	0.05	0.1
Acenaphthylene	0.02	0.04	Di-n-Octyl Phthalate	0.05	0.1
Anthracene	0.02	0.04	Fluoranthene	0.02	0.04
Benzo(a)Anthracene	0.02	0.04	Fluorene	0.02	0.04
Benzo(a)Pyrene	0.02	0.04	Indeno(1,2,3-cd)Pyrene	0.02	0.04
Benzo(b)Fluoranthene	0.02	0.04	Naphthalene	0.02	0.04
Benzo(g,h,i)Perylene	0.02	0.04	Pentachlorophenol	0.2	0.4
Benzo(k)Fluoranthene	0.02	0.04	Phenanthrene	0.02	0.04
Benzyl Alcohol	0.1	0.2	Phenol	0.1	0.2
Benzyl Butyl Phthalate	0.1	0.2	Pyrene	0.02	0.04
Bis(2-Ethylhexyl)Phthalate	0.05	0.1	Bis(2-ethylhexyl)adipate	0.1	0.2
Caffeine	0.02	0.04	Bisphenol A	0.25	0.5
Chrysene	0.02	0.04	Total 4-Nonylphenol	0.1	0.2

NOTE: The MDL/RDL limits are calculated on a 1 liter extraction to a final volume of 1 ml. MDL/RDL limits will vary depending on amount extracted and final volume.

As with the PCB congeners, field blanks will be collected by decanting KCEL supplied DI water from a carboy through the autosampler to the receiving vessel. These blanks will be conducted in the field and delivered to the laboratory with environmental samples. Additionally, the following QC samples will be evaluated:

- A **method blank** is an aliquot of a clean reference matrix (deionized, distilled water for water samples) that is processed through the entire analytical procedure. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results for all target analytes should be "less than the MDL."
- A **laboratory duplicate** is a second aliquot of sample matrix that split from the original autosampler composite. The laboratory duplicate is processed through the entire analytical procedure along with the original sample in the same quality control batch. Laboratory duplicate results are used to assess the precision of the analytical method.
- A **spike blank** is to be analyzed with each QC sample batch. The OPR samples must show acceptable recoveries, according to Table X below, in order to samples to be analyzed and data to be reported.

Acceptance criteria for SVOC analysis are as shown in Table 6 below. Note that matrix spikes and spike duplicates for SVOCs are a priority and shall be conducted before sample material is utilized for metals or conventionals analysis.

Table 7. SVOC QA/QC Frequency and Acceptance Criteria

Parameter	Method Blank, 1 per Extraction batch ¹	Spike Blank (% Recovery) 1 per Extraction batch ²	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)
Phenol	<MDL		50-150	100
1,4-Dichlorobenzene	<MDL		50-150	100
Naphthalene	<MDL		50-150	100
Pentachlorophenol	<MDL		50-150	100
Acenaphthylene	<MDL		50-150	100
Acenaphthene	<MDL	46-118	46-118	100
Fluorene	<MDL		50-150	100
Phenanthrene	<MDL		50-150	100

Parameter	Method Blank, 1 per Extraction batch ¹	Spike Blank (% Recovery) 1 per Extraction batch ²	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)
Anthracene	<MDL		50-150	100
Fluoranthene	<MDL		50-150	100
Pyrene	<MDL	26-127	26-127	100
Benzo(a)anthracene	<MDL		50-150	100
Chrysene	<MDL		50-150	100
Benzo(b)fluoranthene	<MDL		50-150	100
Benzo(k)fluoranthene	<MDL		50-150	100
Benzo(a)pyrene	<MDL		50-150	100
Indeno(1,2,3-Cd)Pyrene	<MDL		50-150	100
Dibenzo(a,h)anthracene	<MDL		50-150	100
Benzo(g,h,i)perylene	<MDL		50-150	100
2-Methylnaphthalene	<MDL		50-150	100
Dimethyl Phthalate	<MDL	50-150	50-150	100
Diethyl Phthalate	<MDL	50-150	50-150	100
Di-N-Butyl Phthalate	<MDL	50-150	50-150	100
Benzyl Butyl Phthalate	<MDL	50-150	50-150	100
Bis(2-Ethylhexyl)Phthalate	<MDL	50-150	50-150	100
Di-N-Octyl Phthalate	<MDL	50-150	50-150	100
Benzyl Alcohol	<MDL		50-150	100
4-Methylphenol	<MDL		50-150	100
Caffeine	<MDL		50-150	100
Total 4-Nonylphenol	<MDL		30-150	100
Bisphenol A	<MDL		30-150	100

Parameter	Method Blank, 1 per Extraction batch ¹	Spike Blank (% Recovery) 1 per Extraction batch ²	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)
Bis(2-ethylhexyl)adipate	<MDL		30-150	100

¹ Only the parameters shown below are added to spikes for routine BNA testing. All target parameters are evaluated in the method blank.

² Extraction batch = 20 samples or less prepared within a 12 hour shift

4.3 Metals

Metals samples will be preserved with ultrapure HNO₃ to a pH less than 2. Arsenic, copper, lead, zinc and additional ancillary metals will be analyzed by ICP-MS. Mercury will be analyzed by CVAA, mid-range. The following detection limits are required (Tables 7 and 8).

Table 8. Trace Metals Target Analytes and Detection Limits (ug/L) by Method EPA 200.8 (ICP-MS)

Analyte	MDL	RDL
As	0.5	2.5
Ca	20	100
Cd	0.1	0.5
Cr	0.4	2
Cu	0.4	2
Fe	20	100
Pb	0.2	1
Mn	0.2	1
Mg	20	100
Ni	0.3	1.5
Ag	0.2	1
Zn	0.5	2.5

Table 9. Trace Metals Target Analytes and Detection Limits (ug/L) Method EPA 245.1 (CVAA)

Analyte / Range	MDL	RDL
Mercury-/ Mid Range	0.05	0.15

Quality control samples shall be within the following limits, although matrix spikes and spike blanks will only be conducted if sufficient sample material is available.

Table 10. Trace Metals QA/QC Frequency and Acceptance Criteria for Water Samples

	Method Blank 1 per batch*	Lab Duplicate (RPD) 1 per batch*	Spike Blank (% Recovery) 1 per batch*	Matrix Spike (% Recovery) 1 per batch*	LCS (% Recovery) 1 per batch*	SRM (% Recovery) 1 per batch* (if available)
Total & Dissolved Metals by ICP-MS	< MDL	RPD ≤ 20%	85 – 115%	70% - 130%	80 - 120%	NA
Total Mercury / CVAA	< MDL	NA	85 – 115%	70% - 130%	NA	80 - 120%

< MDL = less than the Method Detection Limit.

RPD = Relative Percent Difference

LCS = Lab Control Sample

NA = Not Applicable

4.4 Conventionals

All conventional analyses will follow Standard Methods (SM) protocols (American Public Health Association [APHA] 1998). Table 10 presents the analytical methods, detection limits and units for conventional analyses.

Table 11. Conventionals Analytical Methods and Detection Limits in mg/L

Analyte	Method	MDL	RDL
Dissolved Organic Carbon	SM5310-B	0.5	1.0
Total Organic Carbon	SM5310-B	0.5	1.0

Analyte	Method	MDL	RDL
Total Suspended Solids	SM2540-D	0.5	1.0
Volatile Suspended Solids	SM 2540E	0.5	1.0
Chemical Oxygen Demand	SM5220D	10	20
Ammonia Nitrogen	SM4500-NH3-G	0.01	0.02
Nitrate+Nitrite Nitrogen	SM4500-NO3-F	0.02	0.04
Total Phosphorus	SM4500-P-B,F	0.005	0.01
Total Nitrogen	SM4500-N-C	0.05	0.10
Alkalinity	SM2320-B	1	10

Dissolved and total organic carbon will be analyzed according to SM5310-B, which is a high-temperature combustion with infrared spectroscopy. Total suspended solids analyses will be performed according to SM2540-D, which is a gravimetric determination. Table 11 describes the minimum QC required for the conventional analysis.

Table 12. Conventional QA/QC Frequency and Acceptance Criteria for Water Samples

Frequency	Method Blank 1 per batch*	Lab Duplicate (RPD) 1 per batch*	Spike Blank (% Recovery) 1 per batch*	Matrix Spike (% Recovery) 1 per batch*	LCS (% Recovery) 1 per batch*	Check Standard (% Recovery) per batch*
Ammonia Nitrogen	<MDL	20%	80-120%	75-125%	85-115%	N/A
Chemical Oxygen Demand	<MDL	25%	80-120%	75-125%	85-115%	N/A
Nitrate+Nitrite Nitrogen	<MDL	20%	80-120%	75-125%	85-115%	N/A
Total Phosphorus	<MDL	20%	80-120%	75-125%	85-115%	N/A
Total Nitrogen	<MDL	20%	80-120%	75-125%	85-115%	N/A

Frequency	Method Blank 1 per batch*	Lab Duplicate (RPD) 1 per batch*	Spike Blank (% Recovery) 1 per batch*	Matrix Spike (% Recovery) 1 per batch*	LCS (% Recovery) 1 per batch*	Check Standard (% Recovery) per batch*
Total Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%	N/A
Dissolved Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%	N/A
Total Suspended Solids	<MDL	25%	N/A	N/A	80-120%	N/A
Volatile Suspended Solids	<MDL	25%	N/A	N/A	N/A	N/A
Alkalinity	NA	10%	N/A	NA	85-115%	N/A

* batch = 20 samples or less prepared as a set

< MDL = less than the Method Detection Limit.

RPD = Relative Percent Difference

LCS = Lab Control Sample

N/A = Not Applicable

Quality control samples analyzed in association with conventional analyses will include method blanks, laboratory duplicates, and matrix spikes. Conventional QC samples will be analyzed at the frequency of one per QC batch, which will generally be up to seven samples for each sampling event during this survey.

- A **method blank** is an aliquot of a clean reference matrix (deionized, distilled water for water samples) that is processed through the entire analytical procedure. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results for all target analytes should be “less than the MDL” for all conventional analyses.
- A **laboratory duplicate** is a second aliquot of sample matrix that is processed through the entire analytical procedure along with the original sample in the same quality control batch. For conventional analyses, the laboratory duplicate aliquots are all analyzed on matrix taken from a single sample container, with the exception of TOC. Laboratory duplicate results are used to assess the precision of the analytical method and the relative percent difference of the results should be within method-specified or performance-based quality control limits.

- A **matrix spike** is a known concentration of one or more target analytes, which is introduced into a second aliquot of one analytical sample. The spiked sample is processed through the entire analytical procedure. Analysis of the matrix spike is used as an indicator of sample matrix effect on the recovery of target analytes and, thus, potential bias introduced into the sample results. Quality control limits are based on the percent recovery of the spiked compounds and are either method-specific or performance-based.

Tables 6, 9, and 11 above detail the frequencies of QC samples required. In general, for all methods except the PCB congener analysis, this frequency is 1 in 20 samples or 1 per batch, whichever is more frequent.

5.0. DATA VALIDATION, REPORTING, AND RECORD KEEPING

Due to the specialized, contracted, methods employed for the PCB analysis, KCEL will conduct additional data validation on the PCB congener data. The other data will receive standard KCEL validation but full documentation will be maintained in the file should more detailed, external review be necessary.

5.1 Data Validation

Data validation is critical for evaluating how well analytical data meet project DQOs. Data validation is performed, at some level, during several steps in the process of sample analysis. Data validation will be performed by the King County Lab QA Officer for this survey by reviewing complete data packages supplied both by Axys Analytical and the King County Environmental Laboratory. PCB congener, SVOCs and metals analytical data from this survey will be validated according to EPA protocols (EPA 2001 and 2004), as appropriate. EPA data validation guidelines are not available for conventional water quality data. Conventional data will be validated against reference method requirements and the QC requirements provided in this SAP. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records. PCB congener data will be flagged as appropriate according to EPA method specific guidance.

5.2 Reporting

All data and supporting information will be available for review upon request. Analytical data reports may be requested, either in hard copy or electronic formats, in Microsoft Excel spreadsheets. Data validation memoranda will be available, either hard copy or electronically, in Microsoft Word format. All other project information will be available for review in hard copy only.

5.3 Record Keeping

All hard-copy field sampling records, custody documents, raw lab data, and laboratory summaries and narratives will be archived according to King County Environmental Laboratory policy for a minimum of ten years from the date samples were collected. These records will include both hard copy and electronic data received from Axys Analytical. Conventional, Trace Metals and Trace Organics analytical data produced by the King County Environmental Laboratory will be maintained on its LIMS database in perpetuity. PCB congener data produced by Axys Analytical will be loaded onto the lab data servers that have tape back up and also maintained in hard copy.

6.0. REFERENCES

- APHA 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. American Public Health Association. Washington, D.C.
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